

## PATENT ABSTRACTS OF JAPAN

(11)Publication number : 07-142578

(43)Date of publication of application : 02.06.1995

(51)Int.Cl.

H01L 21/768

H01L 21/316

(21)Application number : 05-306996

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(22)Date of filing : 15.11.1993

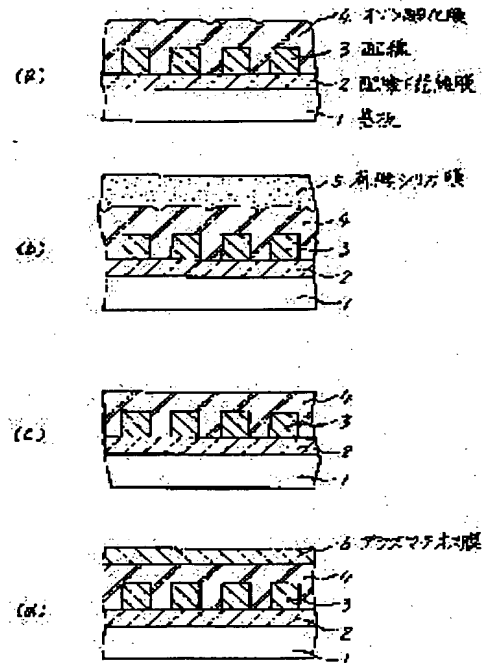
(72)Inventor : KUBO TORU

## (54) SEMICONDUCTOR DEVICE AND MANUFACTURE THEREOF

## (57)Abstract:

PURPOSE: To form an inter-layer insulating film of high reliability without a plasma treatment performed at the time of forming an inter-layer insulating film on a wiring.

CONSTITUTION: An ozone oxide film 4 is formed on the surface including a wiring 3 provided on a semiconductor substrate 1 by an organic silane ozone series normal pressure CVD method in which ozone is reacted to an organic alkoxyl silane including at least one straight chain polysiloxane combination, and an organic silica film 5 is applied thereto with spin coating, and after that, the whole part of the organic silica film 5 and the surface of the ozone oxide film 4 are flattened by etching-back with reactivity ion-etching, and a plasma dioside film 6 is formed thereon by an organic silane plasma CVD method. The inter-layer insulating film is constituted mainly of the ozone oxide film 5, so that a plasma treatment is not required and the burying quality between wirings may be improved to increase reliability of the inter-layer insulating film.



## LEGAL STATUS

[Date of request for examination] 29.03.1994

[Date of sending the examiner's decision of rejection] 19.08.1997

[Kind of final disposal of application other than the examiner's decision of rejection or application converted registration]

[Date of final disposal for application]

[Patent number]

[Date of registration]

[Number of appeal against examiner's decision of rejection]

[Date of requesting appeal against examiner's decision of rejection]

[Date of extinction of right]

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**CLAIMS**

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**[Claim(s)]**

[Claim 1] In the semiconductor device which has wiring formed on the semi-conductor substrate, and the interlayer insulation film formed on said semi-conductor substrate including this wiring said interlayer insulation film The 1st oxidation silicone film formed with the organic silane ozone system ordinary pressure CVD method to which ozone and organic alkoxysilane including siloxane association of the shape of one or more straight chain were made to react, The semiconductor device characterized by having the 2nd oxidation silicone film formed on this 1st oxidation silicone film by the organic silane plasma-CVD method by which the laminating was carried out.

[Claim 2] The 1st oxidation silicone film is a semiconductor device of claim 1 with which it comes to carry out flattening of the front face.

[Claim 3] The semiconductor device of claims 1 or 2 which have the lower layer oxidation silicone film formed in the lower layer of the 1st oxidation silicone film depending on the method of organic silane plasma CVD.

[Claim 4] The process which forms the 1st oxidation silicone film in a front face including wiring formed on the semi-conductor substrate with the organic silane ozone system ordinary pressure CVD method to which ozone and organic alkoxysilane including siloxane association of the shape of one or more straight chain were made to react, The process which carries out the etching back of all of said organic silica film, and the front face of said 1st silicon oxide film by reactive ion etching, and carries out flattening after carrying out spin spreading of the organic silica film on said 1st silicon oxide film, The manufacture approach of the semiconductor device characterized by including the process which forms the 2nd oxidation silicone film by the organic silane plasma-CVD method on said 1st oxidation silicone film.

[Claim 5] The manufacture approach of the semiconductor device of claim 4 including the process which forms a lower layer oxidation silicone film by the organic silane plasma-CVD method on the front face of a semi-conductor substrate including wiring before forming the 1st oxidation silicone film.

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## DETAILED DESCRIPTION

## [Detailed Description of the Invention]

[0001]

[Industrial Application] This invention relates to the structure and its manufacture approach of the interlayer insulation film especially about the semiconductor device with which the interlayer insulation film is formed in wiring.

[0002]

[Description of the Prior Art] Detailed-ization of the wiring width of face formed on a semi-conductor substrate and a wiring pitch dimension is advanced with high integration of a semiconductor device in recent years. For this reason, in case the coverage nature in the edge of wiring poses a problem and the interlayer insulation film formed on this wiring constitutes multilayer-interconnection structure, flattening of the top face of an interlayer insulation film comes to be required. For example, in JP,3-123029,A and JP,3-278435,A, what constituted the interlayer insulation film from an oxidation silicone film (the ozone TEOSU film is called hereafter) formed of the reaction of organic alkoxysilane and ozone is proposed. However, in order that this ozone TEOSU film might present a remarkable substrate dependency (reference T.IEE Japan, 652, VOL.111-A, NO.7 (1991)), when it was made to deposit on the part where it carries out [ that an oxidation silicone film is formed on wiring, etc. and ], and the tooth space between wiring is made minute, it had the trouble that a void occurred by connection of overhanging in a wiring edge. Moreover, since there were more film Nakamizu daily doses than the silicon oxide film formed by the plasma-CVD method, there was also a problem of degrading a device property. In order to conquer this problem, the measures which carry out plasma treatment of the substrate oxidation silicone film before ozone TEOSU film formation are taken.

[0003] Drawing 6 (a) - (d) is the sectional view having shown the conventional semiconductor device with which such measures were taken in order of the production process. First, as shown in drawing 6 (a), on a silicon substrate 21, the BPSG film which is a bottom insulator layer of wiring is deposited and heat-treated, and an insulator layer 22 is formed. On this insulator layer 22, patterning of the aluminum film containing copper and silicon is deposited and carried out to the thickness of 1 micrometer, and wiring 23 is formed. furthermore, the plasma chemistry vapor growth (CVD) which uses an ethyl silicate [Si (OC two H5)4] (TEOS is called hereafter) as a raw material on a front face including wiring 23 -- the oxidation silicone film (the plasma TEOSU film is called hereafter) 24 formed using law is deposited on the thickness of 0.4 micrometers. Furthermore, it is for [ N2 ] 1 minute on it at the conditions of RF frequency 13.56MHZ, power 200W, and pressure 1.0torr. Plasma treatment is performed (reference: J.Electrochem.Soc., Vol.139, No.6, June 1992).

[0004] Next, as shown in drawing 6 (b), the oxidation silicone film (the ozone TEOSU film is

called hereafter) 25 formed using the ozone ordinary pressure vapor growth which uses TEOS as a raw material is deposited on the thickness of 0.8 micrometers. Furthermore, on this ozone TEOSU film 25, the spin applying method is used and the organic silica film 26 is formed at the thickness of about 1 micrometer. Next, as shown in drawing 6 (c), the etching back of the whole surface is carried out using a parallel plate mold batch type reactive ion etching system on conditions to which the etching rate of the ozone TEOSU film 25 and the organic silica film 26 becomes almost equal, and flattening of the front face is carried out. Finally, as shown in drawing 6 (d), the plasma TEOSU film 27 is deposited on the ozone TEOSU film 25 at the thickness of 0.4 micrometers. Thereby, the interlayer insulation film with which flattening of the front face was carried out is formed.

[0005]

[Problem(s) to be Solved by the Invention] With this conventional semiconductor device, it is the front face of the plasma TEOSU film N2. Since plasma treatment is carried out, the surface dry area of the ozone TEOSU film can be inhibited, and the membranous quality of the ozone TEOSU film formed on it and embeddability can be improved (2 (1992) Kubo, the collection of Ikeda, a swamp, and the 39th applied-physics relation union lecture meeting lecture drafts, 596, No. the Society of Chemical Engineers, Japan CVD extraordinarily finishing [Kubo / a lecture] on seminar mini symposium October 22, 1992 : University of Tokyo). Moreover, N2 It becomes possible to reduce the amount of OH radicals in the film by FURAZUMA processing. However, it is N2 to the plasma TEOSU film. There is a problem that a process becomes long by adding plasma treatment. Moreover, these N2 The margin of plasma treatment conditions is small and the problem of being bad also has process stability. The object of this invention is to offer the semiconductor device which made it possible to reduce the amount of OH radicals in the film, and to improve the film room and embeddability as an interlayer insulation film, and its manufacture approach, without performing plasma treatment.

[0006]

[Means for Solving the Problem] The semiconductor device of this invention consists of the 1st oxidation silicone film formed with the organic silane ozone system ordinary-pressure CVD method to which the organic alkoxysilane which includes siloxane association of the one or more shape of ozone and a straight chain for the interlayer insulation film for insulating wiring prepared on the semi-conductor substrate is made to react, and the 2nd oxidation silicone film formed on this 1st oxidation silicone film by the organic silane plasma-CVD method by which the laminating was carried out. Moreover, it considers as the configuration which has the lower layer oxidation silicone film formed in the lower layer of the 1st oxidation silicone film depending on the method of organic silane plasma CVD. The process which forms the 1st oxidation silicone film in a front face including wiring which established the manufacture approach of the semiconductor device of this invention on the semi-conductor substrate with the organic silane ozone system ordinary pressure CVD method to which ozone and organic alkoxysilane including siloxane association of the shape of one or more straight chain are made to react, The process which carries out the etching back of all of said organic silica film, and the front face of said 1st silicon oxide film by reactive ion etching, and carries out flattening after carrying out spin spreading of the organic silica film on this 1st silicon oxide film, Since the process which forms the 2nd oxidation silicone film by the organic silane plasma-CVD method on said 1st oxidation silicone film is included, it is. Moreover, before forming the 1st oxidation silicone film, the process which forms a lower layer oxidation silicone film by the organic silane plasma-CVD method on the front face of a semi-conductor substrate including wiring is included.

[0007]

[Function] Since the ozonate film is formed as 1st oxidation silicone film using organic alkoxysilane and ozone including siloxane association of the shape of one or more straight chain and this is constituted from this invention as some interlayer insulation films, the interlayer insulation film in which a configuration and membraneous quality excel the conventional TEOS film is obtained. That is, since at least one siloxane association exists, the binding fraction of Si-OH to Si-O after a reaction becomes small, the amount of OH radicals in the film decreases, and membraneous quality improves. Since there are few amounts of OH radicals and this reaction intermediate deposits and carries out the flow also of the reaction intermediate to homogeneity on wiring and the plasma oxidation film (all are canal nature), it can embed between wiring without a void and a substrate dependency (a surface dry area, pattern dependency) becomes moreover, less remarkable [ the reaction intermediate ] on wiring and the plasma oxidation film. For this reason, with constituting the ozonate film as an interlayer insulation film, even if it does not use the plasma treatment to the plasma TEOSU film, a configuration and membraneous quality can be raised. Moreover, since there are few amounts of OH radicals in the film, direct wiring can be made to accumulate, and a highly reliable interlayer insulation film can be formed more.

[0008]

[Example] Next, this invention is explained with reference to a drawing. Drawing 1 (a) - (d) is the sectional view of the semiconductor device in which one example of this invention was shown in order of the process. First, on silicon substrate top 1, as shown in drawing 1 (a), after depositing the BPSG film on the thickness of 0.5 micrometers with an ordinary pressure CVD method, heat treatment for 30 minutes is performed in 900-degree C nitrogen-gas-atmosphere mind, and the bottom insulator layer 2 of wiring is formed. Next, on the bottom insulator layer 2 of said wiring, the aluminum film containing copper and silicon is deposited by the thickness of 1 micrometer by the sputtering method, patterning of this is carried out, and wiring 3 is formed. Next, a parallel plate mold single-wafer-processing atmospheric pressure CVD system is used for a front face-including-said-wiring 3, and it deposits with the ordinary pressure CVD method in the conditions of the substrate temperature of 400 degrees C, organic alkoxysilane flow rate 50SCCM, and ozone flow rate 400SCCM, the 1st oxidation silicone film 4, i.e., ozonate film, with a thickness of 0.8 micrometers.

[0009] Said organic alkoxysilane is a compound which has one or more straight chain-like association [ siloxane ] in drawing 2 like the hexa ethoxy disiloxane which shows a structure expression here, and the general formula is as follows.

$\text{Si}_n\text{O}_{n-12}(\text{OC two H}_5)_n$  however  $n \geq 2$ , and said ozonate film are oxide films which this organic alkoxysilane and ozone were made to react with an ordinary pressure CVD method, and formed them.

[0010] Then, as shown in drawing 1 (b), the organic silica film 5 is formed by the thickness of about 1 micrometer by the spin applying method on said ozonate film 4. Furthermore, as shown in drawing 1 (c), a parallel plate mold batch type reactive ion etching system is used, and it is  $\text{CF}_4$ . Quantity-of-gas-flow 100SCCM and  $\text{O}_2$  Quantity-of-gas-flow 15SCCM, pressure 0.1torr, frequency 13.56MHZ, and high-frequency power 0.3W/cm<sup>2</sup> On conditions, the organic silica film 5 all reaches and the etching back of a part of front face of the ozonate film 4 is carried out. Thereby, flattening of the front face of the left-behind ozonate film 4 is carried out. In addition, the etching rate of the ozonate film 4 is made almost the same as the etching rate of the organic silica film 5, or it enlarges a little. Finally, as shown in drawing 1 (d), it deposits by the

thickness of 0.4 micrometers on the ozonate film 4 by which flattening was carried out by the organic silane plasma-CVD method for having used parallel plate mold single-wafer-processing plasma-CVD equipment, the 2nd oxidation silicone film 6, i.e., plasma TEOSU film.

[0011] Thus, with the formed interlayer insulation film, the surface dry area of the ozonate film 4 is conventional N2. Compared with the case where it forms using a plasma treatment technique, it is controlled more than comparable, and membraneous quality can be improved. Moreover, only the part for which wiring spacing does not use the ozone TEOSU film in the device below 0.6-micrometer rule does not have generating of a void, either, and good embedding nature is obtained. Furthermore, the thing which put the ozone TEOSU film on the ozonate film of this invention, and the conventional plasma TEOSU film which carried out plasma treatment at drawing 3, As what put the ozone TEOSU film is compared and shown in the conventional plasma TEOSU film which has not carried out plasma treatment, by what was used as the interlayer insulation film, the ozonate film of this invention There are few OH radical contents in the ozonate film than the thing of the conventional interlayer insulation film, and it turns out that the membraneous quality in this point is also improving.

[0012] Moreover, drawing 4 shows the aluminum pattern dependency of the thickness at the time of forming two sorts of above mentioned conventional interlayer insulation films, and the interlayer insulation film of this invention to what formed the bottom insulator layer 12 of wiring in the silicon substrate 11, and formed the aluminum wiring 13 on it. When having processed nothing on the substrate plasma TEOSU film 14, the ozone TEOSU film 15 grown up on it shows an aluminum pattern dependency, and uniform film formation is difficult for drawing 4 (a). Moreover, drawing 4 (b) is N2. The ozone TEOSU film 15 can be formed on substrate plasma TEOSU film 14' which performed plasma treatment, and the ozone TEOSU film 15 can be grown up into homogeneity. Furthermore, drawing 4 (c) forms the ozonate film 16 of this invention, and uniform film growth is possible for it similarly. At this point, by this invention, although it is comparable as the thing of drawing 4 (b), since uniform film formation can be performed in an ozonate film independent, without using the substrate plasma TEOSU film in this invention, it becomes advantageous in respect of the cutback of manufacture processes. In addition, as drawing 3 showed, since there are few amounts of OH radicals in the film, the ozonate film of this invention is because the aluminum pattern dependency is not almost remarkable in a high ozone level field, either.

[0013] Drawing 5 (a) - (d) is the sectional view of the semiconductor device in which other examples of this invention are shown in order of a process. First, on a silicon substrate 1, as shown in drawing 5 (a), after depositing the BPSG film on the thickness of 0.5 micrometers with an ordinary pressure CVD method, heat treatment for 30 minutes is performed in 900-degree C nitrogen-gas-atmosphere mind, and the bottom insulator layer 2 of wiring is formed. Next, on the bottom insulator layer 2 of wiring, the aluminum film containing copper and silicon is deposited by the thickness of 1 micrometer by the sputtering method, and carries out patterning, and wiring 3 is formed. Next, parallel plate single-wafer-processing plasma-CVD equipment is used for a front face including wiring 3, and it deposits on it by the thickness of 0.4 micrometers by the organic silane plasma-CVD method, lower layer oxidation silicone film 7, i.e., plasma TEOSU film. And on it, further, a parallel plate mold single-wafer-processing atmospheric pressure CVD system is used, and it deposits with the ordinary pressure CVD method in the conditions of the substrate temperature of 400 degrees C, organic alkoxysilane flow rate 50SCCM, and ozone flow rate 400SCCM, the 1st oxidation silicone film 4, i.e., ozonate film, with a thickness of 0.8 micrometers.

[0014] Then, as shown in drawing 5 (b), the organic silica film 5 is formed by the thickness of about 1 micrometer by the spin applying method on the ozonate film 4. Furthermore, as shown in drawing 5 (c), a parallel plate mold batch type reactive ion etching system is used, and it is CF<sub>4</sub>. Quantity-of-gas-flow 100SCCM and O<sub>2</sub> Quantity-of-gas-flow 15SCCM, pressure 0.1torr, frequency 13.56MHZ, and high-frequency power 0.3W/cm<sup>2</sup> On conditions, the organic silica film 5 all reaches, the etching back of a part of front face of the ozonate film 4 is carried out, and flattening of the front face of the ozonate film 4 is carried out. Here, the etching rate of the ozonate film 4 is made almost the same as the etching rate of the organic silica film 5, or it enlarges a little. Finally, as shown in drawing 5 (d), it deposits by the thickness of 0.4 micrometers on the ozonate film 4 by which flattening was carried out by the organic silicon plasma-CVD method for having used parallel plate mold single-wafer-processing plasma-CVD equipment, the 2nd oxidation silicone film 6, i.e., plasma TEOSU film.

[0015] In this configuration, since an interlayer insulation film is the configuration which carried out the laminating of the plasma TEOSU film and the ozonate film to three layers, can constitute as an interlayer insulation film which employed each advantage of the plasma TEOSU film and the ozonate film efficiently, suppression of the substrate dependency (a surface dry area, pattern dependency) to reduction of the amount of OH radicals in the film of an interlayer insulation film, the plasma TEOSU film, etc. and the cutback of plasma treatment processes are attained, and formation of a highly reliable interlayer film realizes it.

[0016]

[Effect of the Invention] As explained above, since this invention constitutes to the subject the ozonate film formed with the organic silane ozone system ordinary pressure CVD method as an interlayer insulation film, it can improve the membraneous quality of an interlayer insulation film, and can improve the embedded nature of a between [ wiring ]. Moreover, since there are few amounts of OH radicals in the film, direct wiring can be made to accumulate. Thereby, suppression of generating of a void, improvement in membraneous quality, suppression of an aluminum pattern dependency, and the routing counter cutback of interlayer film formation are attained, and formation of a highly reliable interlayer film is attained. There is effectiveness which can form a highly reliable interlayer insulation film more. Moreover, since the manufacture approach of this invention forms the ozonate film with an organic silane ozone system ordinary pressure CVD method on wiring, and performs flattening using the organic silica film on it and should just form the plasma TEOSU film on it, its plasma treatment is unnecessary and it can realize simplification of a manufacture process.

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**DESCRIPTION OF DRAWINGS**

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**[Brief Description of the Drawings]**

**[Drawing 1]** It is the sectional view showing one example of this invention in order of a production process.

**[Drawing 2]** It is the structure expression of the hexa ethoxy disiloxane which is one of the organic alkoxysilane.

**[Drawing 3]** It is drawing comparing and showing OH absorption coefficient in the film in the insulator layer between each class of this invention and the conventional technique.

**[Drawing 4]** It is drawing comparing and showing the aluminum pattern dependency of the insulator layer between each class of this invention and the conventional technique.

**[Drawing 5]** It is the sectional view showing other examples of this invention in order of a production process.

**[Drawing 6]** It is the sectional view showing the production process of the conventional interlayer insulation film in order of a process.

**[Description of Notations]**

1 Semi-conductor Substrate

2 Bottom Insulator Layer of Wiring

3 Wiring

4 Ozonate Film (1st Oxidation Silicone Film)

5 Organic Silica Film

6 Plasma TEOSU Film

7 Plasma TEOSU Film

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**[Translation done.]**



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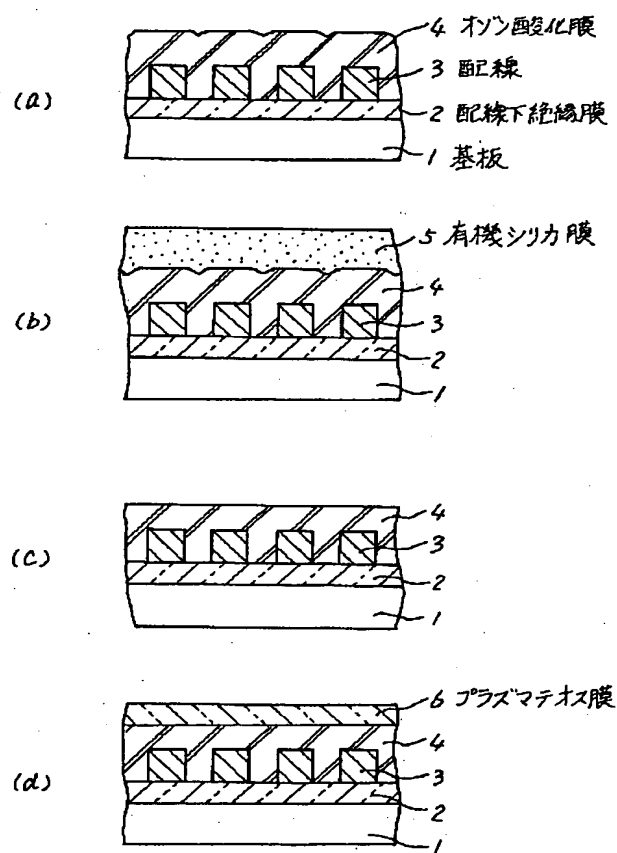
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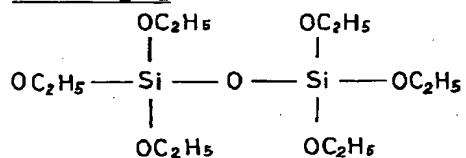
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## DRAWINGS

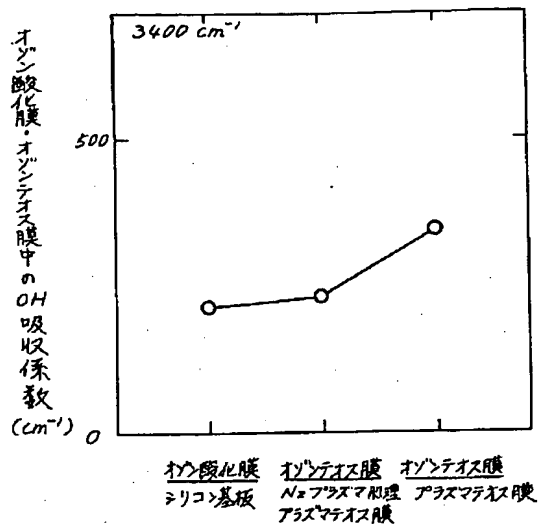
[Drawing 1]



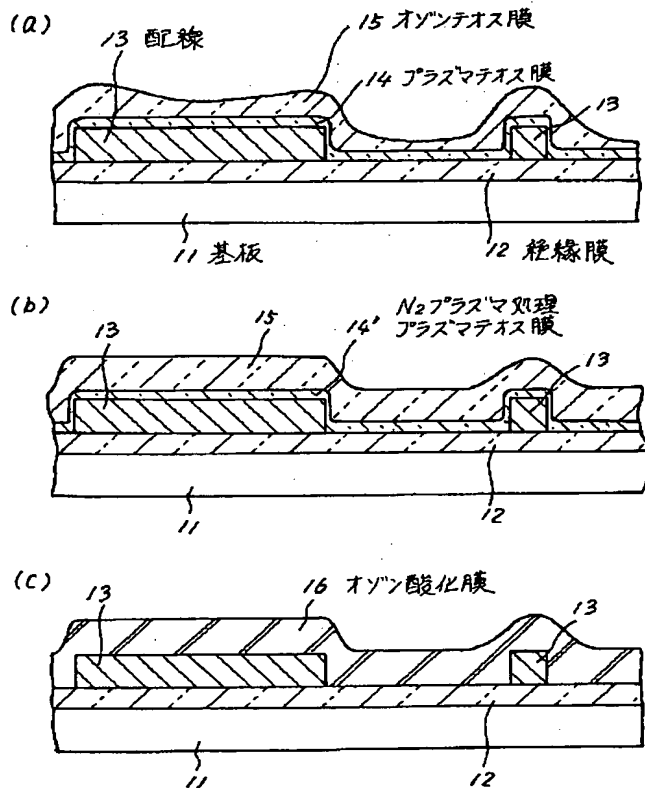
[Drawing 2]



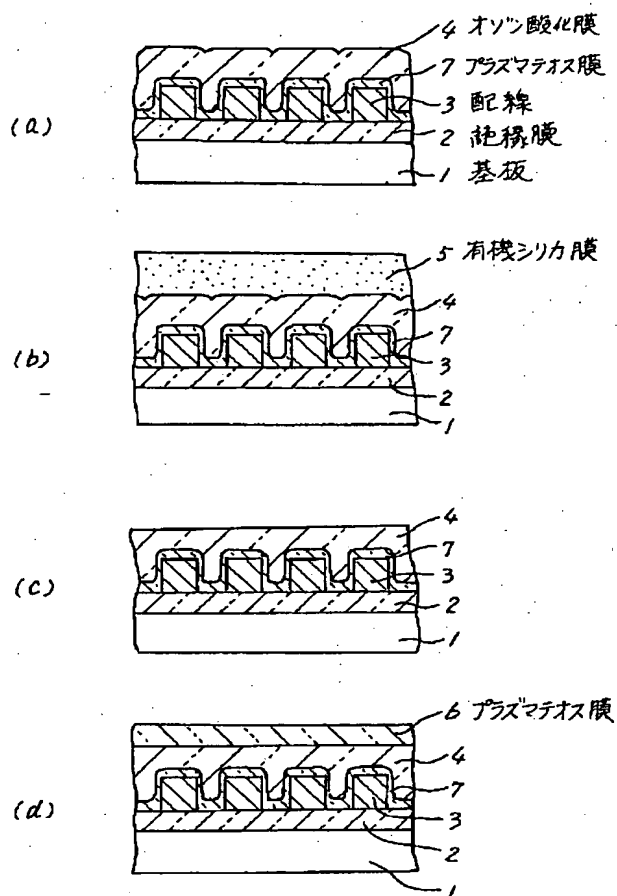
[Drawing 3]



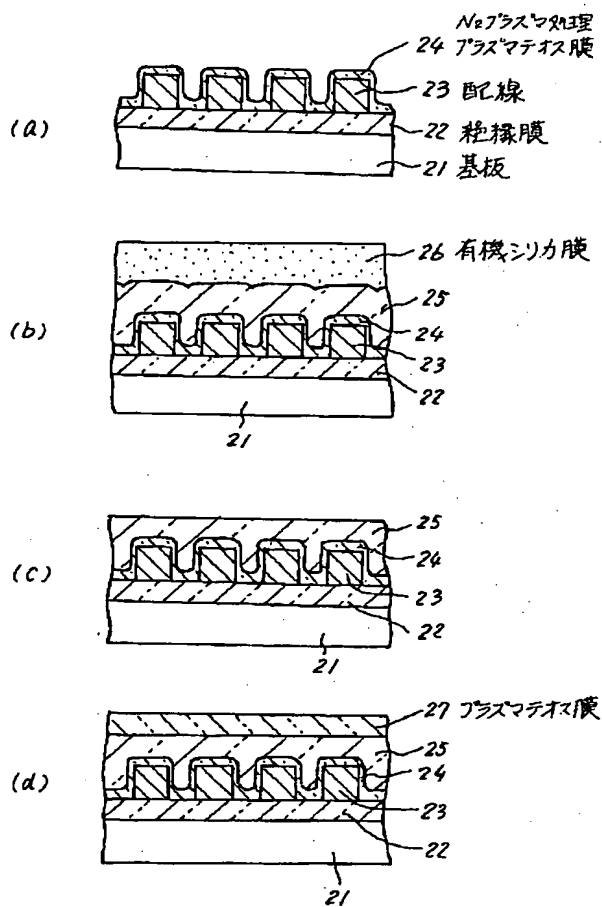
[Drawing 4]



[Drawing 5]



[Drawing 6]



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**WRITTEN AMENDMENT**


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----- [procedure amendment]

[Filing Date] September 22, Heisei 6

[Procedure amendment 1]

[Document to be Amended] Description

[Item(s) to be Amended] Claim 3

[Method of Amendment] Modification

[Proposed Amendment]

[Claim 3] The semiconductor device of claims 1 or 2 which have the lower layer oxidation silicone film formed in the lower layer of the 1st oxidation silicone film by the organic silane plasma-CVD method.

[Procedure amendment 2]

[Document to be Amended] Description

[Item(s) to be Amended] 0006

[Method of Amendment] Modification

[Proposed Amendment]

[0006]

[Means for Solving the Problem] The semiconductor device of this invention consists of the 1st oxidation silicone film formed with the organic silane ozone system ordinary-pressure CVD method to which the organic alkoxysilane which includes siloxane association of the one or more shape of ozone and a straight chain for the interlayer insulation film for insulating wiring prepared on the semi-conductor substrate is made to react, and the 2nd oxidation silicone film formed on this 1st oxidation silicone film by the organic silane plasma-CVD method by which the laminating was carried out. Moreover, it considers as the configuration which has the lower layer oxidation silicone film formed in the lower layer of the 1st oxidation silicone film by the organic silane plasma-CVD method. The process which forms the 1st oxidation silicone film in a front face including wiring which established the manufacture approach of the semiconductor device of this invention on the semi-conductor substrate with the organic silane ozone system ordinary pressure CVD method to which ozone and organic alkoxysilane including siloxane association of the shape of one or more straight chain are made to react, The process which carries out the etching back of all of said organic silica film, and the front face of said 1st silicon oxide film by reactive ion etching, and carries out flattening after carrying out spin spreading of the organic silica film on this 1st silicon oxide film, The process which forms the 2nd oxidation silicone film by the organic silane plasma-CVD method on said 1st oxidation silicone film is included. Moreover, before forming the 1st oxidation silicone film, the process which forms a

lower layer oxidation silicone film by the organic silane plasma-CVD method on the front face of a semi-conductor substrate including wiring is included.

[Procedure amendment 3]

[Document to be Amended] Description

[Item(s) to be Amended] 0007

[Method of Amendment] Modification

[Proposed Amendment]

[0007]

[Function] Since the ozonate film is formed as 1st oxidation silicone film using organic alkoxysilane and ozone including siloxane association of the shape of one or more straight chain and this is constituted from this invention as some interlayer insulation films, the interlayer insulation film in which a configuration and membraneous quality excel the conventional TEOS film is obtained. That is, since at least one siloxane association exists, the binding fraction of Si-OH to Si-O after a reaction becomes small, the amount of OH radicals in the film decreases, and membraneous quality improves. Since there are few amounts of OH radicals and this reaction intermediate deposits and carries out the flow also of the reaction intermediate to homogeneity on wiring and the plasma oxidation film (all are hydrophobicity), it can embed between wiring without a void and a substrate dependency (a surface dry area, pattern dependency) becomes moreover, less remarkable [ the reaction intermediate ] on wiring and the plasma oxidation film. For this reason, with constituting the ozonate film as an interlayer insulation film, even if it does not use the plasma treatment to the plasma TEOSU film, a configuration and membraneous quality can be raised. Moreover, since there are few amounts of OH radicals in the film, direct wiring can be made to accumulate, and a highly reliable interlayer insulation film can be formed more.

[Procedure amendment 4]

[Document to be Amended] Description

[Item(s) to be Amended] 0012

[Method of Amendment] Modification

[Proposed Amendment]

[0012] Moreover, drawing 4 shows the aluminum pattern dependency of the thickness at the time of forming two sorts of above mentioned conventional interlayer insulation films, and the interlayer insulation film of this invention to what formed the bottom insulator layer 12 of wiring in the silicon substrate 11, and formed the aluminum wiring 13 on it. When having processed nothing on the substrate plasma TEOSU film 14, the ozone TEOSU film 15 grown up on it shows an aluminum pattern dependency, and uniform film formation is difficult for drawing 4 (a). Moreover, drawing 4 (b) is N2. The ozone TEOSU film 15 can be formed on substrate plasma TEOSU film 14' which performed plasma treatment, and the ozone TEOSU film 15 can be grown up into homogeneity. Furthermore, drawing 4 (c) forms the ozonate film 16 of this invention, and uniform film growth is possible for it similarly. At this point, by this invention, although it is comparable as the thing of drawing 4 (b), since uniform film formation can be performed in an ozonate film independent, without using the substrate plasma TEOSU film in this invention, it becomes advantageous in respect of the cutback of manufacture processes. In addition, as drawing 3 showed the ozonate film of this invention, since there are few amounts of OH radicals in the film, an aluminum pattern dependency is hardly remarkable also in a high ozone level field.

[Translation done.]

(19) 日本国特許庁 (J P)

(12) 公開特許公報 (A)

(11) 特許出願公開番号

特開平7-142578

(43) 公開日 平成7年(1995)6月2日

(51) Int.Cl. <sup>8</sup>	識別記号	庁内整理番号	F I	技術表示箇所
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21/316	X	7352-4M		
	M	7352-4M		
			H 0 1 L 21/ 90	M
審査請求 有 請求項の数 5 F D (全 7 頁)				

(21) 出願番号 特願平5-306996

(22) 出願日 平成5年(1993)11月15日

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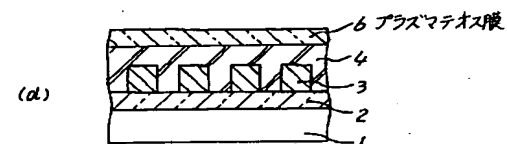
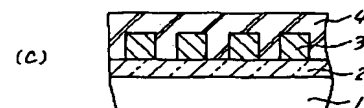
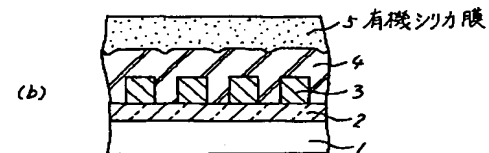
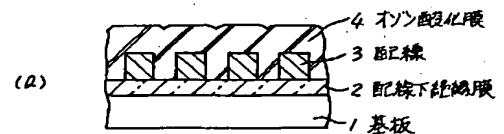
(74) 代理人 弁理士 鈴木 章夫

## (54) 【発明の名称】 半導体装置及びその製造方法

## (57) 【要約】

【目的】 配線上の層間絶縁膜を形成する際にプラズマ処理を行うことなく、高信頼性の層間絶縁膜の形成が可能な半導体装置とその製造方法を得る。

【構成】 半導体基板1上に設けた配線3を含む表面に、オゾンと1つ以上の直鎖状のシロキサン結合を含む有機アルコキシシランとを反応させる有機シラン・オゾン系常圧CVD法によりオゾン酸化膜4を形成し、この上に有機シリカ膜5をスピン塗布した後、反応性イオンエッチングにより有機シリカ膜5の全部と前記オゾン酸化膜4の表面をエッチングバックして平坦化し、その上に有機シランプラズマCVD法によりプラズマテオス膜6を形成する。オゾン酸化膜5を主体に層間絶縁膜を構成することで、プラズマ処理が不要となり、かつ配線間での埋込性を改善し、層間絶縁膜の信頼性を向上する。





## 【特許請求の範囲】

【請求項1】 半導体基板上に形成された配線と、この配線を含む前記半導体基板上に形成された層間絶縁膜とを有する半導体装置において、前記層間絶縁膜は、オゾンと1つ以上の直鎖状のシロキサン結合を含む有機アルコキシシランとを反応させた有機シラン・オゾン系常圧CVD法により形成した第1の酸化シリコン膜と、この第1の酸化シリコン膜の上に積層された有機シランプラズマCVD法により形成された第2の酸化シリコン膜とを備えることを特徴とする半導体装置。

【請求項2】 第1の酸化シリコン膜は、表面が平坦化されてなる請求項1の半導体装置。

【請求項3】 第1の酸化シリコン膜の下層に、有機シランプラズマCVD法により形成された下層酸化シリコン膜を有する請求項1または2の半導体装置。

【請求項4】 半導体基板上に形成した配線を含む表面にオゾンと1つ以上の直鎖状のシロキサン結合を含む有機アルコキシシランとを反応させた有機シラン・オゾン系常圧CVD法により第1の酸化シリコン膜を形成する工程と、前記第1の酸化シリコン膜の上に有機シリカ膜をスピン塗布した後、反応性イオンエッチングにより前記有機シリカ膜の全部と前記第1の酸化シリコン膜の表面をエッチングバックして平坦化する工程と、前記第1の酸化シリコン膜の上に有機シランプラズマCVD法により第2の酸化シリコン膜を形成する工程を含むことを特徴とする半導体装置の製造方法。

【請求項5】 第1の酸化シリコン膜を形成する前に、配線を含む半導体基板の表面上に有機シランプラズマCVD法により下層の酸化シリコン膜を形成する工程を含む請求項4の半導体装置の製造方法。

## 【発明の詳細な説明】

## 【0001】

【産業上の利用分野】 本発明は配線に層間絶縁膜が形成されている半導体装置に関し、特にその層間絶縁膜の構造及びその製造方法に関する。

## 【0002】

【従来の技術】 近年の半導体装置の高集積化に伴い、半導体基板上に形成される配線幅及び配線ピッチ寸法の微細化が進められている。このため、この配線上に形成される層間絶縁膜は、配線の縁部でのカバレッジ性が問題となり、多層配線構造を構成する際に層間絶縁膜の上面の平坦化が要求されるようになる。例えば、特開平3-123029号公報、特開平3-278435号公報では、有機アルコキシシランとオゾンとの反応によって形成される酸化シリコン膜（以下、オゾンテオス膜と称する）で層間絶縁膜を構成したものが提案されている。しかし、このオゾンテオス膜は顕著な下地依存性（参考文献T. IEE Japan, 652, VOL. 111-A, NO. 7 (1991)）を呈するため、配線上に酸化シリコン膜が形成される等して配線間スペースが微小

とされている箇所に堆積させると、配線縁部でのオーバーハング同士の接続によってボイドが発生するという問題点があった。また、プラズマCVD法により形成される酸化シリコン膜よりも膜中水分量が多いのでデバイス特性を劣化させるという問題もあった。この問題を克服するためにオゾンテオス膜形成前に、下地酸化シリコン膜をプラズマ処理する対策がとられている。

【0003】 図6(a)～(d)はこのような対策がとられた従来の半導体装置を製造工程順に示した断面図である。まず、図6(a)に示すように、シリコン基板21の上に配線下絶縁膜であるBPSG膜を堆積して熱処理し、絶縁膜22を形成する。この絶縁膜22の上に銅、シリコンを含有するアルミニウム膜を1 $\mu$ mの厚さに堆積してパターニングし、配線23を形成する。更に、配線23を含む表面にケイ酸エチル〔Si(OC<sub>2</sub>H<sub>5</sub>)<sub>2</sub>〕（以下、TEOSと称する）を原料とするプラズマ化学気相成長（CVD）法を用いて形成される酸化シリコン膜（以下、プラズマテオス膜と称する）24を0.4 $\mu$ mの厚さに堆積する。更に、その上に、RF周波数13.56MHz、パワー200W、圧力1.0torrの条件で、1分間N<sub>2</sub>プラズマ処理を施す（参考文献：J. Electrochem. Soc., Vol. 139, No. 6, June 1992）。

【0004】 次に、図6(b)に示すように、TEOSを原料とするオゾン常圧気相成長法を用いて形成される酸化シリコン膜（以下、オゾンテオス膜と称する）25を0.8 $\mu$ mの厚さに堆積する。更に、このオゾンテオス膜25の上にスピン塗布法を用いて有機シリカ膜26を約1 $\mu$ mの厚さに形成する。次に、図6(c)に示すように、平行平板型バッチ式反応性イオンエッチング装置を用いて、オゾンテオス膜25と有機シリカ膜26のエッチングレートがほぼ等しくなるような条件で全面をエッチングバックし、表面を平坦化する。最後に、図6(d)に示すように、オゾンテオス膜25の上にプラズマテオス膜27を0.4 $\mu$ mの厚さに堆積する。これにより、表面が平坦化された層間絶縁膜が形成される。

## 【0005】

【発明が解決しようとする課題】 この従来の半導体装置では、プラズマテオス膜の表面をN<sub>2</sub>プラズマ処理しているために、オゾンテオス膜の表面荒れを抑止でき、その上に形成するオゾンテオス膜の膜質、埋込み性を向上できる（久保・池田・沼沢・第39回応用物理学関係連合講演会講演予稿集、596, No. 2 (1992)、化学工学会CVD特別研究会ミニシンポジウム1992年10月22日にて久保が講演済：東京大学）。また、N<sub>2</sub>プラズマ処理により膜中OH基量を低減することが可能となる。しかしながら、プラズマテオス膜に対してN<sub>2</sub>プラズマ処理を加えることでプロセスが長くなるという問題がある。また、このN<sub>2</sub>プラズマ処理条件のマージンが小さく、プロセス安定性が悪いという問題もあ

る。本発明の目的は、プラズマ処理を行うことなく、膜中OH基量を低減し、かつ層間絶縁膜としての膜室や埋込み性を改善することを可能にした半導体装置とその製造方法を提供することにある。

#### 【0006】

【課題を解決するための手段】本発明の半導体装置は、半導体基板上に設けた配線を絶縁するための層間絶縁膜を、オゾンと1つ以上の直鎖状のシロキサン結合を含む有機アルコキシシランとを反応させる有機シラン・オゾン系常圧CVD法により形成した第1の酸化シリコン膜と、この第1の酸化シリコン膜の上に積層された有機シランプラズマCVD法により形成された第2の酸化シリコン膜とで構成する。また、第1の酸化シリコン膜の下層に、有機シランプラズマCVD法により形成された下層酸化シリコン膜を有する構成とする。本発明の半導体装置の製造方法は、半導体基板上に設けた配線を含む表面にオゾンと1つ以上の直鎖状のシロキサン結合を含む有機アルコキシシランとを反応させる有機シラン・オゾン系常圧CVD法により第1の酸化シリコン膜を形成する工程と、この第1の酸化シリコン膜の上に有機シリカ膜をスピン塗布した後、反応性イオンエッチングにより前記有機シリカ膜の全部と前記第1の酸化シリコン膜の表面をエッチングバックして平坦化する工程と、前記第1の酸化シリコン膜の上に有機シランプラズマCVD法により第2の酸化シリコン膜を形成する工程を含むものである。また、第1の酸化シリコン膜を形成する前に、配線を含む半導体基板の表面上に有機シランプラズマCVD法により下層の酸化シリコン膜を形成する工程を含む。

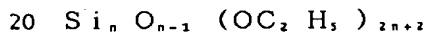
#### 【0007】

【作用】本発明では、1つ以上の直鎖状のシロキサン結合を含む有機アルコキシシランとオゾンを用いて第1の酸化シリコン膜としてオゾン酸化膜を形成し、これを層間絶縁膜の一部として構成しているため、従来のTEOS膜よりも形状、膜質が優れている層間絶縁膜が得られる。即ち、シロキサン結合が少なくとも1つ存在しているので、反応後のSi-Oに対するSi-OHの結合比が小さくなり、膜中のOH基量が減少し、膜質が向上する。また、反応中間体でもOH基量は少ないので、この反応中間体が配線上やプラズマ酸化膜上（いずれも疎水性）に均一に堆積し、フローするので、配線間をボイドなく埋め込むことができ、配線上やプラズマ酸化膜上で下地依存性（表面荒れ、パターン依存性）が顕著でなくなる。このため、オゾン酸化膜を層間絶縁膜として構成することで、プラズマテオス膜に対するプラズマ処理を用いなくても形状、膜質を向上させることができる。また、膜中OH基量が少ないので直接配線に堆積させることができ、より高信頼性の層間絶縁膜を形成することができる。

#### 【0008】

【実施例】次に、本発明について図面を参照して説明する。図1(a)～(d)は、本発明の一実施例を工程順に示した半導体装置の断面図である。まず、図1(a)に示すように、シリコン基板上1の上に、常圧CVD法によりBPSSG膜を0.5μmの厚さに堆積した後、900℃の窒素ガス雰囲気中で30分間の熱処理を行い配線下絶縁膜2を形成する。次に、前記配線下絶縁膜2の上に銅及びシリコンを含有するアルミニウム膜をスパッタリング法により1μmの厚さに堆積し、これをパターニングして配線3を形成する。次に、前記配線3を含む表面に平行平板型枚葉式常圧CVD装置を用い、基板温度400℃、有機アルコキシシラン流量50SCCM、オゾン流量400SCCMの条件での常圧CVD法により厚さ0.8μmの第1の酸化シリコン膜、即ちオゾン酸化膜4を堆積する。

【0009】ここで、前記有機アルコキシシランは図2に構造式を示すヘキサエトキシジシロキサンのように、直鎖状のシロキサン結合を1つ以上もつ化合物であり、一般式は次の通りである。



但し、 $n \geq 2$

そして、前記オゾン酸化膜は、この有機アルコキシシランとオゾンとを常圧CVD法により反応させて形成した酸化膜である。

【0010】続いて、図1(b)に示すように、前記オゾン酸化膜4の上にスピン塗布法により有機シリカ膜5を約1μmの厚さで形成する。更に、図1(c)に示すように、平行平板型バッチ式反応性イオンエッチング装置を用い、CF<sub>4</sub>ガス流量100SCCM、O<sub>2</sub>ガス流量15SCCM、圧力0.1torr、周波数13.56MHz、ならびに高周波電力0.3W/cm<sup>2</sup>の条件で、有機シリカ膜5の全部及びオゾン酸化膜4の表面の一部をエッチングバックする。これにより、残されたオゾン酸化膜4の表面が平坦化される。なお、オゾン酸化膜4のエッチングレートと有機シリカ膜5のエッチングレートとをほぼ同じにするか、又はやや大きくする。最後に、図1(d)に示すように、平坦化されたオゾン酸化膜4の上に平行平板型枚葉式プラズマCVD装置を用いた有機シランプラズマCVD法により第2の酸化シリコン膜、即ちプラズマテオス膜6を0.4μmの厚さで堆積する。

【0011】このように形成された層間絶縁膜では、オゾン酸化膜4の表面荒れは、従来のN<sub>2</sub>プラズマ処理技術を用いて形成した場合と比べて同程度以上に抑制されており、膜質が改善できる。また、配線間隔が0.6μmルール以下のデバイスにおいても、オゾンテオス膜を用いない分だけボイドの発生もなく、良好な埋め込み性が得られる。更に、図3に本発明のオゾン酸化膜と、従来のプラズマ処理したプラズマテオス膜にオゾンテオス膜を被着したものと、従来のプラズマ処理していないブ

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ラズマテオス膜にオゾンテオス膜を被着したものとを比較して示すように、本発明のオゾン酸化膜を層間絶縁膜としたものでは、従来の層間絶縁膜のものよりもオゾン酸化膜中のOH基含有量は少なく、この点での膜質も向上していることがわかる。

【0012】また、図4はシリコン基板11に配線下絶縁膜12を形成し、その上にアルミニウム配線13を形成したのに対して、前記した従来の2種の層間絶縁膜と本発明の層間絶縁膜を形成した際の膜厚のアルミパターン依存性を示すものである。図4(a)は下地プラズマテオス膜14に何も処理を施していない時は、その上に成長させるオゾンテオス膜15がアルミパターン依存性を示し、均一な膜形成が困難である。また、図4

(b)はN<sub>2</sub>プラズマ処理を施した下地プラズマテオス膜14'上にオゾンテオス膜15を形成したものであり、均一にオゾンテオス膜15を成長させることができる。更に、図4(c)は本発明のオゾン酸化膜16を形成したものであり、同様に均一な膜成長が可能である。この点で、本発明では図4(b)のものと同程度であるが、本発明では下地プラズマテオス膜を用いることなく、オゾン酸化膜単独で均一な膜形成ができるため、製造プロセスの削減の点で有利となる。なお、本発明のオゾン酸化膜は、図3で示したように膜中OH基量が少ないため、アルミパターン依存性が高オゾン濃度領域でもほとんど顕著でないためである。

【0013】図5(a)~(d)は、本発明の他の実施例を工程順に示す半導体装置の断面図である。まず、図5(a)に示すように、シリコン基板1の上に、常圧CVD法によりBPSG膜を0.5μmの厚さに堆積した後、900℃の窒素ガス雰囲気中で30分間の熱処理を行い配線下絶縁膜2を形成する。次に、配線下絶縁膜2の上に銅及びシリコンを含有するアルミニウム膜をスパッタリング法により1μmの厚さで堆積してパターンニングし、配線3を形成する。次に、配線3を含む表面に平行平板型プラズマCVD装置を用いて有機シランプラズマCVD法により下層の酸化シリコン膜、即ちプラズマテオス膜7を0.4μmの厚さで堆積する。そして、その上に更に、平行平板型プラズマCVD装置を用い、基板温度400℃、有機アルコキシシラン流量50SCCM、オゾン流量400SCCMの条件での常圧CVD法により厚さ0.8μmの第1の酸化シリコン膜、即ちオゾン酸化膜4を堆積する。

【0014】続いて、図5(b)に示すように、オゾン酸化膜4の上にスピン塗布法により有機シリカ膜5を約1μmの厚さで形成する。更に、図5(c)に示すように、平行平板型バッチ式反応性イオンエッチング装置を用い、CF<sub>4</sub>ガス流量100SCCM、O<sub>2</sub>ガス流量15SCCM、圧力0.1torr、周波数13.56MHz、ならびに高周波電力0.3W/cm<sup>2</sup>の条件で、有機シリカ膜5の全部及びオゾン酸化膜4の表面の一部

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をエッチングバックしてオゾン酸化膜4の表面を平坦化する。ここで、オゾン酸化膜4のエッチングレートと有機シリカ膜5のエッチングレートとはほぼ同じにするか、又はやや大きくする。最後に、図5(d)に示すように、平坦化されたオゾン酸化膜4の上に平行平板型枚葉式プラズマCVD装置を用いた有機シリコンプラズマCVD法により第2の酸化シリコン膜、即ちプラズマテオス膜6を0.4μmの厚さで堆積する。

【0015】この構成においては、層間絶縁膜は、プラズマテオス膜とオゾン酸化膜を3層に積層した構成であるため、プラズマテオス膜とオゾン酸化膜のそれぞれの利点を生かした層間絶縁膜として構成でき、層間絶縁膜の膜中OH基量の減少、プラズマテオス膜等への下地依存性(表面荒れ、パターン依存性)の抑止、プラズマ処理工程の削減が可能になり、高信頼性の層間膜の形成が実現する。

【0016】

【発明の効果】以上説明したように本発明は、層間絶縁膜として有機シラン・オゾン系常圧CVD法により形成したオゾン酸化膜を主体に構成しているため、層間絶縁膜の膜質を向上することができ、かつ配線間への埋込性を改善することができる。また、膜中OH基量が少ないので直接配線に堆積させることができる。これにより、ボイドの発生を抑止、膜質の向上、アルミパターン依存性の抑止、層間膜形成の工程数削減が達成され、高信頼性の層間膜の形成が可能になる。より高信頼性の層間絶縁膜を形成することができる効果がある。また、本発明の製造方法は、配線上有機シラン・オゾン系常圧CVD法によりオゾン酸化膜を形成し、その上で有機シリカ膜を用いた平坦化を行い、かつその上にプラズマテオス膜を形成するだけで良いため、プラズマ処理が不要であり、製造プロセスの簡略化が実現できる。

【図面の簡単な説明】

【図1】本発明の一実施例を製造工程順に示す断面図である。

【図2】有機アルコキシシランの1つであるヘキサエトキシジシロキサン(HEOS)の構造式である。

【図3】本発明と従来技術の各層間絶縁膜における膜中OH吸収係数を比較して示す図である。

【図4】本発明と従来技術の各層間絶縁膜のアルミパターン依存性を比較して示す図である。

【図5】本発明の他の実施例を製造工程順に示す断面図である。

【図6】従来の層間絶縁膜の製造工程を工程順に示す断面図である。

【符号の説明】

1 半導体基板

2 配線下絶縁膜

3 配線

4 オゾン酸化膜(第1の酸化シリコン膜)

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40

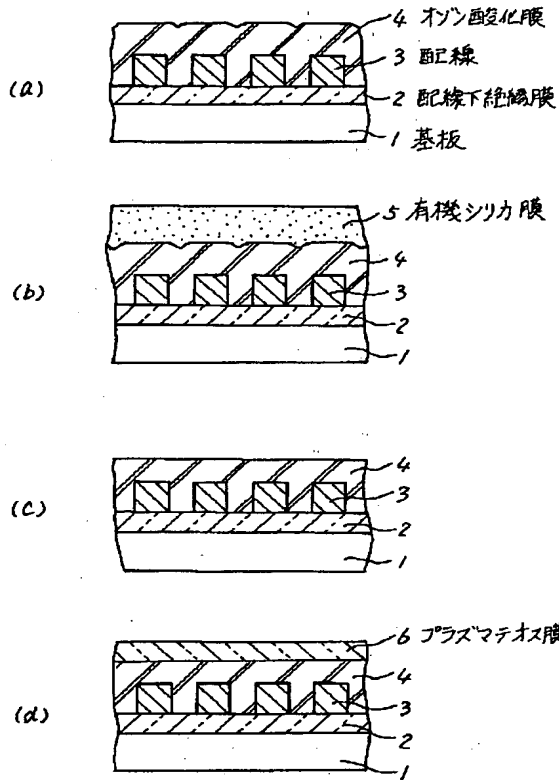
50

- 5 有機シリカ膜  
6 プラズマテオス膜

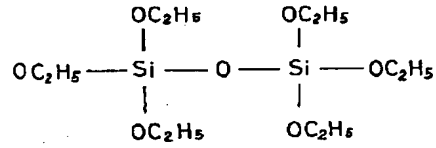
\* 7 プラズマテオス膜

\*

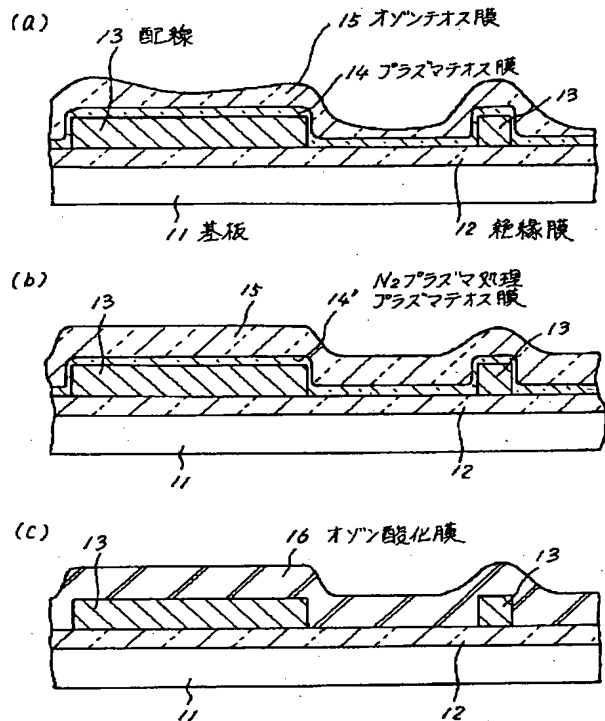
【図1】



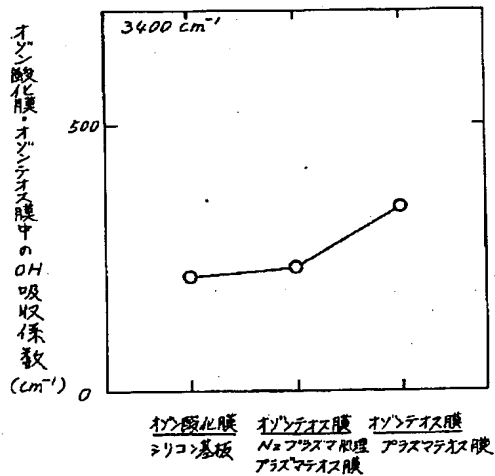
【図2】



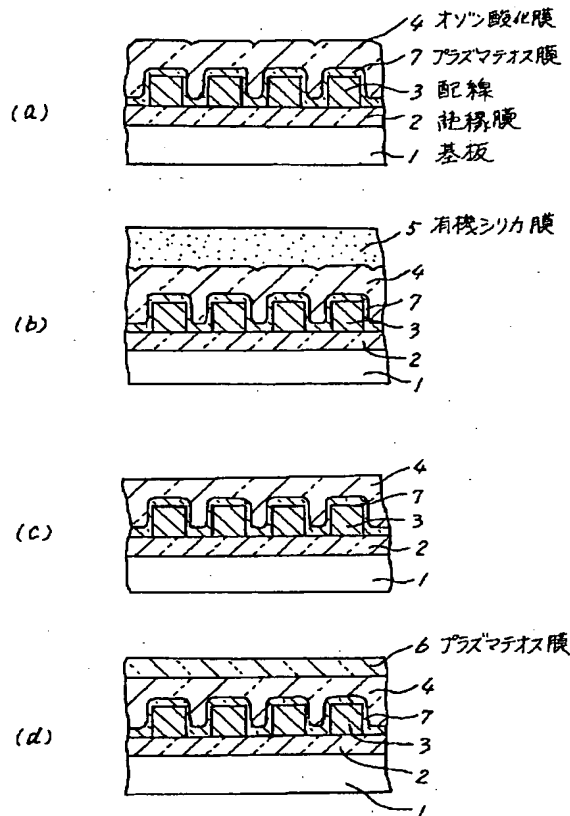
【図4】



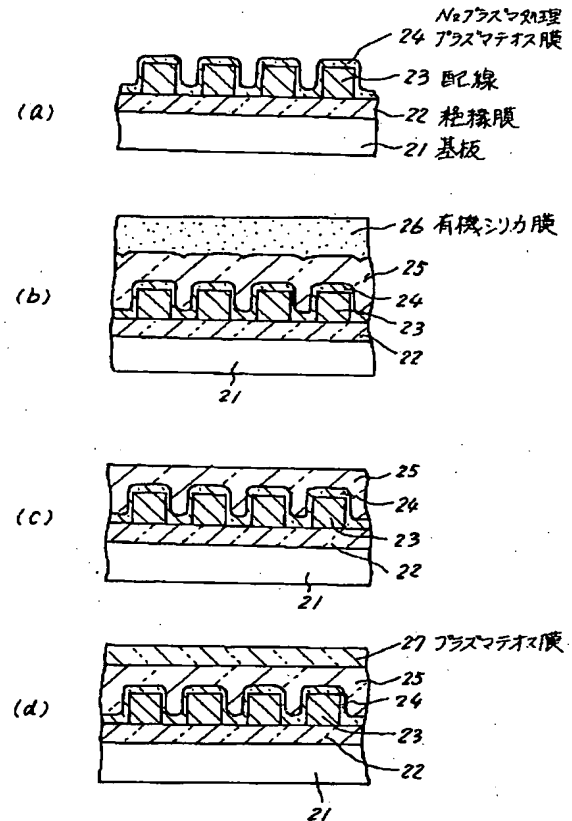
【図3】



【図5】



【図6】



## 【手続補正書】

【提出日】平成6年9月22日

## 【手続補正1】

【補正対象書類名】明細書

【補正対象項目名】請求項3

【補正方法】変更

## 【補正内容】

【請求項3】 第1の酸化シリコン膜の下層に、有機シランプラズマCVD法により形成された下層酸化シリコン膜を有する請求項1または2の半導体装置。

## 【手続補正2】

【補正対象書類名】明細書

【補正対象項目名】0006

【補正方法】変更

## 【補正内容】

【0006】

【課題を解決するための手段】本発明の半導体装置は、半導体基板上に設けた配線を絶縁するための層間絶縁膜を、オゾンと1つ以上の直鎖状のシロキサン結合を含む有機アルコキシシランとを反応させる有機シラン・オゾ

ン系常圧CVD法により形成した第1の酸化シリコン膜と、この第1の酸化シリコン膜の上に積層された有機シランプラズマCVD法により形成された第2の酸化シリコン膜とで構成する。また、第1の酸化シリコン膜の下層に、有機シランプラズマCVD法により形成された下層酸化シリコン膜を有する構成とする。本発明の半導体装置の製造方法は、半導体基板上に設けた配線を含む表面にオゾンと1つ以上の直鎖状のシロキサン結合を含む有機アルコキシシランとを反応させる有機シラン・オゾン系常圧CVD法により第1の酸化シリコン膜を形成する工程と、この第1の酸化シリコン膜の上に有機シリカ膜をスピン塗布した後、反応性イオンエッチングにより前記有機シリカ膜の全部と前記第1の酸化シリコン膜の表面をエッチングバックして平坦化する工程と、前記第1の酸化シリコン膜の上に有機シランプラズマCVD法により第2の酸化シリコン膜を形成する工程を含む。また、第1の酸化シリコン膜を形成する前に、配線を含む半導体基板の表面上に有機シランプラズマCVD法により下層の酸化シリコン膜を形成する工程を含む。

## 【手続補正3】

【補正対象書類名】明細書

【補正対象項目名】0007

【補正方法】変更

【補正内容】

【0007】

【作用】本発明では、1つ以上の直鎖状のシロキサン結合を含む有機アルコキシシランとオゾンを用いて第1の酸化シリコン膜としてオゾン酸化膜を形成し、これを層間絶縁膜の一部として構成しているの、従来のTEOS膜よりも形状、膜質が優れている層間絶縁膜が得られる。即ち、シロキサン結合が少なくとも1つ存在しているので、反応後のSi-Oに対するSi-OHの結合比が小さくなり、膜中のOH基量が減少し、膜質が向上する。また、反応中間体でもOH基量は少ないので、この反応中間体が配線上やプラズマ酸化膜上（いずれも疎水性）に均一に堆積し、フローするので、配線間をボイドなく埋め込むことができ、配線上やプラズマ酸化膜上で下地依存性（表面荒れ、パターン依存性）が顕著でなくなる。このため、オゾン酸化膜を層間絶縁膜として構成することで、プラズマテオス膜に対するプラズマ処理を用いなくても形状、膜質を向上させることができる。また、膜中OH基量が少ないので直接配線に堆積させることができ、より高信頼性の層間絶縁膜を形成することができる。

## 【手続補正4】

【補正対象書類名】明細書

【補正対象項目名】0012

【補正方法】変更

【補正内容】

【0012】また、図4はシリコン基板11に配線下絶縁膜12を形成し、その上にアルミニウム配線13を形成したもののに対して、前記した従来の2種の層間絶縁膜と本発明の層間絶縁膜を形成した際の膜厚のアルミパターン依存性を示すものである。図4(a)は下地プラズマテオス膜14に何も処理を施していない時は、その上に成長させるオゾンテオス膜15がアルミパターン依存性を示し、均一な膜形成が困難である。また、図4

(b)はN<sub>2</sub>プラズマ処理を施した下地プラズマテオス膜14'上にオゾンテオス膜15を形成したものであり、均一にオゾンテオス膜15を成長させることができる。更に、図4(c)は本発明のオゾン酸化膜16を形成したものであり、同様に均一な膜成長が可能である。この点で、本発明では図4(b)のものと同程度であるが、本発明では下地プラズマテオス膜を用いることなく、オゾン酸化膜単独で均一な膜形成ができるため、製造プロセスの削減の点で有利となる。なお、本発明のオゾン酸化膜は、図3で示したように膜中OH基量が少ないため、アルミパターン依存性は高オゾン濃度領域でもほとんど顕著でない。